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Influence of alkali solution on compressive strength of calcined clay and GGBS alkali activated mortar

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ABSTRACT
Calcined clay is presently considered as aluminosilicate source that will extend the application of alkali activated materials (AAM) due to its low embodied energy and global abundance, but its strength performance when cured under ambient conditions depends largely on the calcination process and the mineralogy of the clay *etc.* In this paper, the density, compressive strength and ultrasonic pulse velocity of ambient-cured calcined clay is compared with that of GGBS mortar activated by sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) solutions. Three groups of mixes were tested, group one and two based on varying the alkali solution to the respective binder ratio, while group three mixes are based on activation of the GGBS with different molarities of the NaOH solution from 4 M to 12 M concentration. The results shows that alkali solution to binder ratio of 0.35 gives the highest compressive strength for all the GGBS mortar mixes. Also, the effect of increasing the molarity of the NaOH solution on the strength of the mortar did not show any clear trend implying that the optimum molarity required is such that there is sufficient alkali to complete the reaction and not in excess to disrupt the geopolymerization reaction or insufficient to initiate and satisfy the reaction. The results further show that Na_2SiO_3 solutions enhances the strength of the GGBS mortar more than NaOH solution by enriching the silicate content of the N-A-S-H gel thereby increasing the binding effect.

1. INTRODUCTION

Alkali Activated Materials (AAM) have continued to receive attention as construction materials with lower CO_2 emissions that will further improve sustainability of the construction industry (Scrivener, *et. al.* 2016). The most promising precursors for AAM are Ground Granulated Blast Furnace Slag (GGBS) and Fly Ash (FA) of adequate quality (Provis 2017). However, global supply of these materials is dwindling due to rapid decommissioning of coal thermal power plants in developed nations that generate PFA as a by – product and massive utilization of GGBS as Supplementary Cementitious Material (SCM) for Portland cement. According to (Scrivener, et. al. 2016), calcined clay is presently the material with substantial potential to extend the availability of suitable minerals for AAM.

Previous studies were mostly on utilization of metakaolin as aluminosilicate source but competing demand by different industries for high purity kaolin clay, high cost and intensive purification process are some of the factors limiting its availability to be used as either SCM or precursor for alkali activation (Ding 2017). Calcined clays are presently considered as cost- effective alternative to high purity metakaolin clay and offers greater supply sustainability due to availability of vast clay reserves globally supplemented by clay waste generated by the ceramics industries and from construction projects (Fernandez 2009).

Alkali activation involves release of the aluminate (AlO_2^-) and silicate (SiO_4^{4-}) ions from an alumino-silicate source by reacting with alkali metal ions to produce hydrated of aluminosilicate (R-A-S-H, where R=Na or K) gel that form a solid mass when hardened and used as binder (Brough 2002). The binding phase of calcined clay is almost exclusively aluminosilicate that forms a highly coordinated 3-Dimensional Si-O-Al polymeric network through polycondensation reaction typical of geopolymer binder (Provis 2014). On the other hand, the reaction product of high calcium content aluminosilicate sources such as GGBS is an aluminum substituted hydrate of calcium silicate (C-A-S-H) gel which is similar to the C-S-H gel formed by OPC but has a lower Calcium to Silicate (C:S) ratio, determined in part, by the nature of activator used for the reaction (Bernal et al. 2011). This low C:S increases the strength of the binding phase, due to its high silicate content and is enhanced by the use of silicate-based alkali solutions (Passuello 2017).

Compressive strength is a basic property of mortar that corresponds very strongly with other mechanical and durability properties of paste, mortar and concrete (Deb, *et. al.* 2014). Alkali activated mortars are often reported to have low early strength and high final strength gain at 28 days, depending on the precursors, alkali solution concentration and curing condition *etc* .

In this paper, the effects of different activators, dosage and sodium hydroxide concentration on the density and compressive strength of calcined clay and GGBS alkali activated mortars cured at ambient condition were compared and reported.

2. Materials and Methods

The GGBS used for this study was supplied by Hanson cement ltd UK from their Teesside plant and

is EN 15167-1 standard compliant with the amorphous content more than 95%, volumetric mass density of the particles of 2.92 g/cm^3 and the d50 of 15 µm. The calcined clay was supplied by Banah UK Ltd and was prepared from low purity kaolin clay through thermal treatment, with the particle sizes which are 50% (d50) and 90% (d90) smaller than 5-8 µm and 16-24 µm respectively. It also had 90% reactive elements, specific gravity of 2.89, specific surface (BET) of 75 m^2/g and a loss on ignition of less than 2%. The oxide compositions of the GGBS and calcined clay are presented in table 1.

Table 1: Major oxide compositions (wt. %) of the calcined clay and GGBS

Oxide (% by weight)	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MgO	CaO	LOI
Calcined clay	35.18	25.4	29.6	2.9	1.3	0.9	< 2%
GGBS	29.38	0.36	11.2	0.7	6.9	43.7	2.4

The sharp sand was supplied by local contractor and had particle sizes finer than 4.5 mm sieve size. NaOH reagent grade pellets of 97% purity and aqueous sodium silicate pentahydrate obtained from fisher scientific were used for the preparation of the alkali solution for the various mixes. The sodium silicate solution was prepared such that the quantity of Na_2SiO_3 in the solution is 44.1%.

The mix design was undertaken for the various blends using a GGBS to sand ratio of 0.5 and calcined clay to sand ratio of 1.

Table 2: Samples label and descriptions

Binder	Sample label	Activator	Alkali solution proportion
GGBS	GGBS – 8 M SH	8 M NaOH	Varies from 30 to 50%
GGBS	GGBS – SS	44.1% Na_2SiO_3	Varies from 30 to 50%
GGBS	GGBS – SH (35%)	NaOH of different molarities (4 - 12 M)	35%
Calcined clay	CC – 8 M SH	8 M NaOH	Varies from 80 to 100 %
Calcined clay	CC – SS	44.1% Na_2SiO_3	Varies from 80 to 100%

The alkali solutions were prepared using distilled water 24 hrs prior to mixing. Table 2 provides label and description of the mortar samples, while the various mortar mixes for the three groups are presented in table 3. The mixing of the various mortar mixes was carried out using a 5 Litre Hobart mixer based on the procedure specified by BS EN 196 – 1. The mixes were then placed in the 50 mm x 50 mm steel cubes moulds and compacted uniformly using the vibration table. The samples were then demoulded after 24 hrs and cured in ambient condition at 20 ± 2 °C and 90% relative humidity to limit the effect of carbonation on the samples, as well as avoid lost or gain of moisture. The density of three replicate mortar cubes were determined at 7 and 28 days for the NaOH activated GGBS mixes using a specific gravity balance based on Archimede's principle and the mean density was then computed.

Table 3: Mortar mixtures (kg per m^3)

Group 1	**Sand kg/m^3**	**GGBS – 8 M SH**		**GGBS – 44.1% SS**	
L:B		GGBS kg/m^3	8 M NaOH kg/m^3	GGBS kg/m^3	Na_2SiO_3 kg/m^3
0.3	1227	614	185	614	185
0.35	1209	604	212	605	212
0.4	1191	596	238	596	238
0.45	1174	587	264	587	264
0.5	1157	579	289	579	289
Group 2	**Sand kg/m^3**	**CC – 8 M SH**		**CC – 44.1% SS**	
L:B		CC kg/m^3	8 M NaOH kg/m^3	CC kg/m^3	Na_2SiO_3 kg/m^3
0.8	723	723	579	723	579
0.85	711	711	604	711	604
0.9	698	698	628	698	628
0.95	686	686	652	686	652
1.0	675	675	675	675	675
Group 3		**Fine Agg. Kg/m^3**		**GGBS – SH (35%)**	
Varied Molarity of SH				GGBS kg/m^3	NaOH kg/m^3
4 M SH (SH 16%)		1209		604	212
6 M SH (SH 24%)		1209		604	212
8 M SH (SH 32%)		1209		604	212
10 M SH (SH 40%)		1209		604	212
12 M SH (SH 48%)		1209		604	212

Also, the compressive strength for the three replicate surface-saturated 50 mm x 50 mm GGBS mortar cubes samples for each of the mixes was determined at 7 and 28 days as specified by BS EN 12390 – 3:2009 using an Avery Denison 2000 compression machine with a loading rate of 0.5 MPa/s. Similarly, the strength of the calcined clay mortar samples were tested using the JJ Lloyd testing machine that has a loading rate of 10 N/s to accommodate the lower strength of the samples.

Furthermore, microstructure of the GGBS mortar was probed. Samples cured at 28 days were vacuum dried and fracture surface were examined by Scan Electron Microscopy (SEM) using a Philip XL – 30 instrument.

3. Results and Discussion

3.1 Effect of NaOH concentration on compressive strength of AAM

NaOH concentration ensures the release of silicate and aluminate ions from the cement replacement materials. From the results in figure 1, increasing the concentration of the NaOH solution above 4 M slightly decreases the strength of the NaOH-activated GGBS mortar. This is thought to reflect the high viscosity of the alkaline solution, restricting ion mobility. This may also delay the geopolymerization process and precipitates the C-(N)-A-S-H gel prematurely.

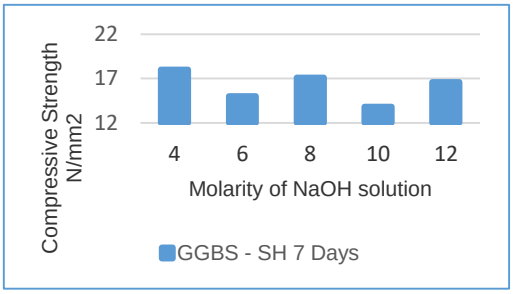

Figure 1: Compressive strength of GGBS mortars activated with various concentration of NaOH solution

3.2 Effect of alkali solution proportion on compressive strength of AAM

Figure 2 shows that the GGBS mortar mixes activated with Na_2SiO_3 solution have significantly higher compressive strength compared to the mixes activated with 8 M NaOH solution due to the higher silicate content of the C-(N)-A-S-H gel precipitated by the Na_2SiO_3 solutions which enhances the strength of the binding phase of the GGBS mortar.

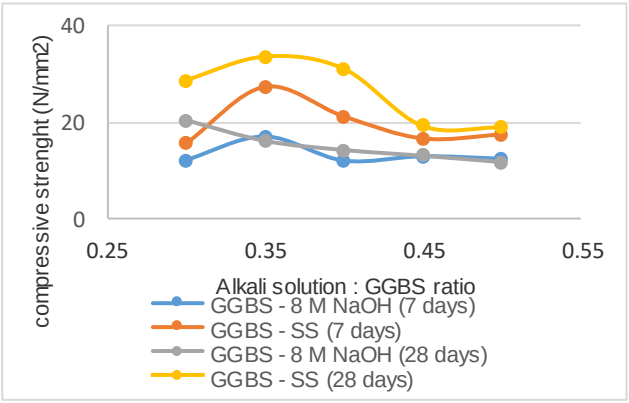

Figure 2: Compressive strength of GGBS mortar activated with different alkali solution to binder ratio for 7 and 28 days curing

The figure 2 result also shows that, the ratio of alkali solution to GGBS of 0.35 produces the highest compressive strength of 27 MPa and 17 MPa at 7 days for the Na_2SiO_3 and NaOH solutions activated mixes respectively. Above 35%, the liquid content in the GGBS mix is high, such that not all the alkali solution was consumed in the reaction. This excess alkali solution results in pores as the mortar dries out thereby causing decreasing strength of the mortar. However, at lower liquid content below 35%, decrease strength is observed due to increase energy required to provide full compaction for the dry mix and inadequate alkali solution that will ensure complete geopolymerization reaction.

Figure 3 shows that significantly higher strength is achieved by activating calcined clay with 8 M NaOH solution compared to the 44.1% Na_2SiO_3 solution due to the greater ability of NaOH solution to release the aluminate and silicate ions from the calcined clay, thereby favouring a more effective geopolymerization reaction which resulted in a stronger binding phase. Also, activation of the calcined clay mortar by NaOH solution favours higher Na_2O/Al_2O_3 molar ratio, while activation by the Na_2SiO_3 solution favours higher SiO_2/Al_2O_3 molar ratio in the geopolymerization reaction. According to Yunsheng *et al.* (2010), Na_2O/Al_2O_3 molar ratios significantly increase the strength of calcined clay based geopolymers compared to SiO_2/Al_2O_3 molar ratios. The results further show that the strength of the calcined clay geopolymer mortar decreases with increase in the proportion of solution above 80% despite the fact that calcined clay requires high amount of solution to produce a homogenous mix due to its high surface area, platy morphology and layered structure.

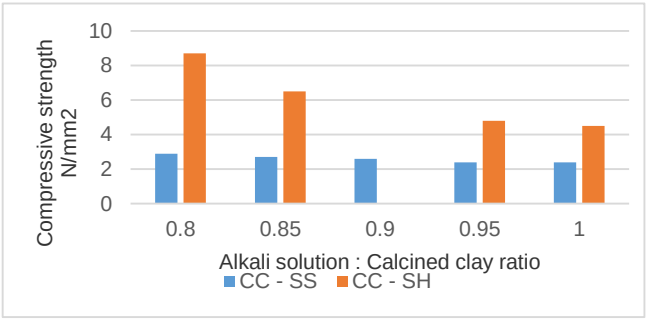

Figure 3: Strength of calcined clay mortar activated with different alkali solution to binder ratio for 7 days curing age

3.3 Relationship between density and compressive strength of GGBS AAM

Figure 4 shows the density of the GGBS mortar mixes decreases due to the increase in proportion of NaOH solution in the mix. Also, density decrease is observed across all the mixes, as the mortar samples dry up from 7 to 28 days. At 7 days, the density of the mortar sample is high due to presence of moisture precipitated by the alkali solution. Furthermore, the highest density of 1352 kg/m^3 recorded for the SH30 shows that NaOH activated GGBS mortar cured under ambient condition is a light weight mortar. Comparing the results presented in figure 2 and 4, a similar trend is observed with respect to compressive strength and density of the mortar mixes. In other words, as the density decreases with increase in proportion of NaOH solution in the GGBS mortar mixes, so too the compressive strength decreases.

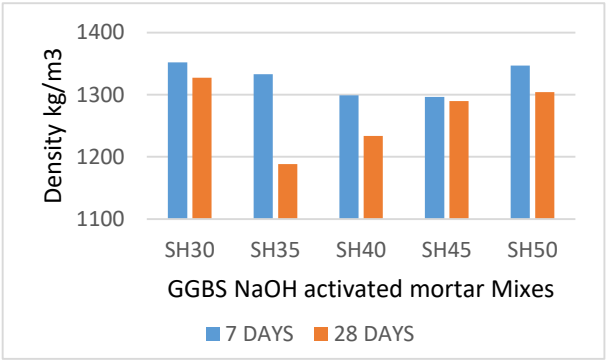

Figure 4: Density of GGBS mortar mixes activated by different proportion of NaOH solution

3.4 Effect of NaOH solution content on Ultrasonic Pulse Velocity of GGBS AAM

The results obtained from the UPV test presented in figure 5 shows a decrease in the computed pulse velocities due to increase in proportion of NaOH solution in the mortar mixes. This further shows that the higher the alkali solution to binder ratio, the greater the amount of pores present in the sample. This phenomenon therefore is the cause of decreasing strength and density as seen in figure 2 and 4 respectively. The UPV results also shows all the mixes fall within the UPV range of 2.5 to 4.5 km/s which is classified as good by the UPV test standard.

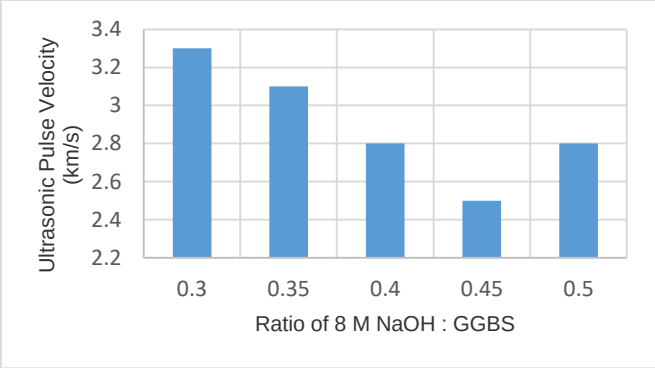

Figure 5: Ultrasonic Pulse Velocity against NaOH: GGBS ratio

3.5 Microstructure of NaOH and Na_2SiO_3 activated GGBS mortar

The microstructure for the GGBS – 8 M NaOH (35%) mortar cured under ambient condition for 28 days presented in figure 6 reveals an undensified and loosely packed structure. The result further shows precipitation of a sponge-like matrix globular unit on the surface with a propagated continuous crack. This uncompacted and porous structure is the cause of decrease strength and low density measured for this mix.

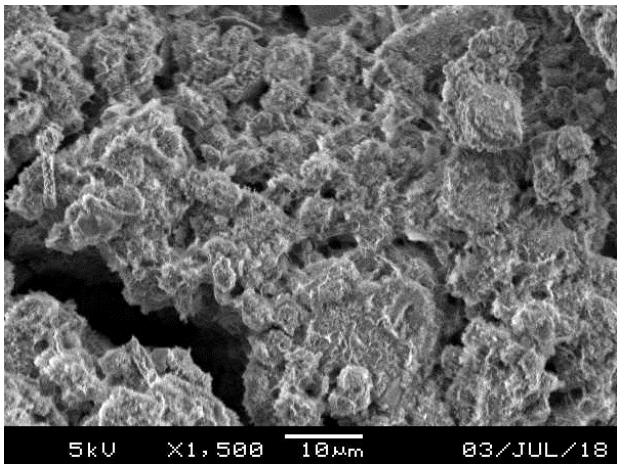

Figure 6: SEM micrograph of 8 M NaOH activated GGBS mortar

The microstructure of the GGBS – SS (35%) mortar cured for 28 days under ambient condition shown in figure 7 reveals a compact matrix that precipitates a hexagonal shape $Ca(OH)_2$ and a dis-ordered tobomorite like C-S-H gel resulting in a high strength mortar as per figure 2.

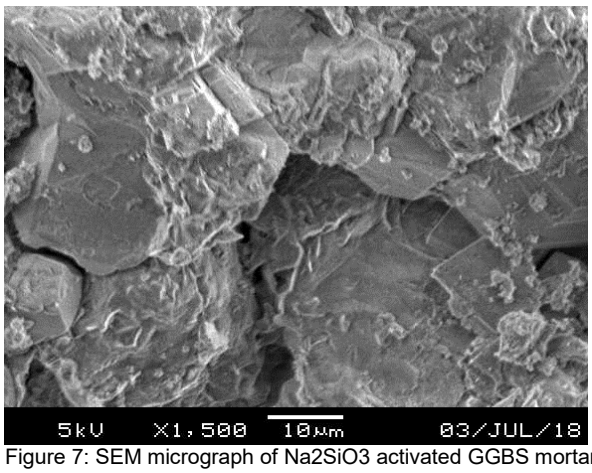

Figure 7: SEM micrograph of Na2SiO3 activated GGBS mortar

4. Conclusions

From the results of this preliminary experimental study, it can be deduced that, significantly higher strength is achieved by utilizing GGBS as aluminosilicate source for mortar cured under ambient conditions compared to calcined clay regardless of the proportion or concentration of the activator used. Also, alkali solution to GGBS ratio of 0.35 gives the highest strength for mortar which has a workable mix, while calcined clay requires a ratio of 0.8 to give its highest strength. NaOH solution influences the strength of the calcined clay mortar more than Na_2SiO_3 solution which is the converse case for the GGBS mortar. Furthermore, a dense and compact binding phase is achieved by activating GGBS with Na_2SiO_3 solution, while a sponge-like matrix that propagate a crack is achieved by NaOH solution activation.

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